

**COMPARISON OF NO<sub>x</sub> REDUCTION TECHNOLOGIES  
FOR INDUSTRIAL APPLICATIONS**

**HAL SHELTON  
SE TECHNOLOGIES, INC.  
BRIDGEVILLE, PA 15017**

**PRESENTED AT:**

**CONFERENCE ON SELECTIVE CATALYTIC & NON-CATALYTIC  
REDUCTION FOR NO<sub>x</sub> CONTROL**

**DEPARTMENT OF ENERGY  
PITTSBURGH ENERGY TECHNOLOGY CENTER  
PITTSBURGH, PA 15236-0940**

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## INTRODUCTION

NO<sub>x</sub> or oxides of nitrogen, has been defined as a criteria pollutant by the Clean Air Act Amendment (CAAA). Mandatory NO<sub>x</sub> reduction is necessary to meet Ozone and ambient air quality limits. Specific reductions of both NO<sub>x</sub> and VOC depends upon Ozone attainment status which is regionally or locally determined.

The CAAA has established environmental limits that have first focused on the utility industry but is now looking for the industrial marketplace to achieve additional NO<sub>x</sub> reductions.

This conference is being held to expand on technology available to meet the various regulated limits.

## NO<sub>x</sub> FORMATION

NO<sub>x</sub> emissions are normally generated by burning fuel and air or through chemical reactions including nitric acid generation, fertilizer production, or other processes that involve nitrogen containing molecules.

Combustion NO<sub>x</sub> (normally called Thermal NO<sub>x</sub>) is formed in high temperature combustion between natural gas (or other fuels) and atmospheric combustion air. The factors affecting thermal NO<sub>x</sub> are:

- Temperature
- Combustion Excess Air
- Burner Design
- Process Application

## PROCESS

Figure 1 illustrates the curve for NO<sub>x</sub> formation. When burning rich (excess fuel) NO<sub>x</sub> is inhibited by insufficient oxygen. Peak NO<sub>x</sub> forms between 5-15% excess air and then drops as the temperature is reduced in accordance with the Zeldovich equilibrium reactions. Burner technology has gone through several transitions to reduce NO<sub>x</sub> emissions. California has led the effort in legislating emission limits for boiler and oil field steamers. The various burner technologies are:

- Staged Air Combustion
- Staged Fuel Combustion
- Flue Gas Recirculation
- Water & Steam injection (minor influence)

Depending upon burner design, staged air and fuel designs reduced NO<sub>x</sub> burning conventional fuels (such as natural gas, etc.) to the following levels:

<u>Design</u>	<u>NO<sub>x</sub> emissions</u>
Conventional	100 PPM
Staged Air	50-60 PPM
Staged Fuel	40-50 PPM

With flue gas recirculation an additional 15-25% reduction can be achieved. These techniques have been successfully used for the past 15 years. Recently (1995-1997), equipment vendors have developed technology that has achieved sub 10 ppm (under controlled conditions) NO<sub>x</sub> emissions while keeping CO and unburned hydrocarbons under 100 ppm. This usually involved premixing natural gas with combustion air and secondary staging with/without flue gas recirculation. A second concept involves gas/air premix with flame diffusion using a porous medium.

Burner technologies have been successfully adapted to boilers (meeting the above limits) using natural gas or other non-nitrogen chemical compounds. Nitrogen containing chemicals that can be found in some gaseous fuels as well as fuel oil and other liquids will significantly increase NO<sub>x</sub> emissions. Figure 2 illustrates how fuel nitrogen will affect NO<sub>x</sub> formation. As shown, a little fuel bound nitrogen goes a long way. Initial work with California oil field steamers burning 0.8% fuel bound nitrogen increased NO<sub>x</sub> emissions by a 2.5 factor over a natural gas design. Flue gas recirculation had less affect upon NO<sub>x</sub> reduction but not compared to that achieved by natural gas. This is because nitrogen bound fuel NO<sub>x</sub> formation is more dependent upon oxygen content and not combustion temperature. Fuel bound NO<sub>x</sub> will be generated at temperatures below 2200°F. This NO<sub>x</sub> will be predominately NO<sub>2</sub>.

Most data has been developed for boiler or boiler type applications (relatively cold surfaces) absorbing heat during the combustion process. What about other applications, such as thermal oxidizers, air heaters, kilns, etc.?

NO<sub>x</sub> emission can be controlled or even reduced for these higher furnace temperature applications using the same techniques by understanding the application and/or selecting the proper technology(s).

In some designs, selection of low NO<sub>x</sub> burner may result in NO<sub>x</sub> emission increases rather than reductions.

Many low NO<sub>x</sub> designs combine staged combustion as well as interstage cooling. Ultimate NO<sub>x</sub> reduction will incorporate staging with SNCR or SCR. The following examples illustrate application of various techniques that minimize NO<sub>x</sub> without needing expensive SNCR or SCR.

A manufacturer of rubber products collected VOC's in an air stream which required a 99%

destruction rate.  $\text{NO}_x$  emissions were limited to less than 0.06 lb/MM BTU (at 1600°F furnace temperature). The oxidizer was combined with an existing waste heat boiler. Table 1 is the test data. The initial design using staged fuel burner did not meet the emissions regulations. Burner air/fuel ratio was changed and 10% natural gas was premixed with the waste vapor. This technology reduced  $\text{NO}_x$  33% (at 1600°F) and met the regulations at 1800°F.

A combined waste chemical plant liquid and vapor oxidizer was required to achieve a 99.99% VOC destruction with  $\text{NO}_x$  less than 0.02 lb/MM BTU. The waste vapor from a process absorber had approximately 8% oxygen and contained both VOC's and CO.

The final design was five control stages. The oxidizer initially operated oxidizing followed by a reducing section, while the remaining three stages progressed from reducing to oxidizing. Operating at 1580°F all objectives were achieved. The design data is found in Table 2.

### **Fertilizer Production**

A government facility had a pilot plant making a fertilizer intermediate reacting elemental phosphorus with nitric acid. Reactor off gas contained up to 130,000 PPM  $\text{NO}_x$ . A 90%  $\text{NO}_x$  reduction was required. Table 3 presents the process data. A two staged thermal reducer was designed. The first stage used a standard burner burning a combination propane,  $\text{NO}_x$  off gas and outside air at 55-60% theoretical air. After reduction, secondary air quenched the gases and oxidized residual, unburned hydrocarbons. Environmental requirements were met. Additional  $\text{NO}_x$  reduction could have been achieved by further staging or injecting ammonia or other urea based chemicals into the second stage.

One final example combined a three stage oxidizer with a waste heat boiler. The wastes being oxidized included hydrogen cyanide, a second liquid waste containing 27% nitrogen and a low oxygen waste vapor with 400-600 PPM  $\text{NO}_x$ . Specific data is found in Table 4. The first stage was oxidizing and the second stage was reducing and cooling using the waste vapor. Secondary re-oxidation air was injected into the third stage. Stack  $\text{NO}_x$  emissions varied between 25 and 125 ppm.

### **SUMMARY**

Extending low  $\text{NO}_x$  burner technology, environmental system suppliers can successfully design low  $\text{NO}_x$  equipment for not only boilers but also high temperature applications. This requires understanding of the fuel compositions, system turndown, and physical design criteria or limitations.

**TABLE 3**

**CHEMICAL PLANT STAGED THERMAL OXIDIZER**

**WASTES:**

**1. ABSORBER OFF GAS**

**515,000 LBS/HR**

**8% OXYGEN**

**0.5% CO**

**0.8% VOC's**

**2. WATER WASTE**

**95% WATER**

**5% RESIDUAL ORGANICS**

**SYSTEM PERFORMANCE**

<b>1. OXIDIZER TEMPERATURE</b>	<b>1580° F</b>
<b>2. STACK OXYGEN</b>	<b>3%</b>
<b>3. NO<sub>x</sub></b>	<b>8-10 PPM (&lt;0.02 LB/MM BTU)</b>
<b>4. AUXILIARY FUEL</b>	<b>60 MM BTU/HR (NOMINAL)</b>
<b>5. VOC DESTRUCTION</b>	<b>99.99%</b>
<b>6. CO</b>	<b>&lt;100 PPM</b>
<b>7. RESIDENCE TIME</b>	<b>1.0 SEC</b>

**TABLE 4**  
**HIGH TECH LOW NO<sub>x</sub> THERMAL**  
**OXIDIZER TEST RESULTS**

	<u>1st stage</u>	<u>Inner Cooling State</u>	<u>Reoxidation Stage</u>
Temp(°F)	2600	1800	1600
Residence Time (sec)	0.6	0.4	1.0
Hydrocarbon (%destruction)			99.99
NO <sub>x</sub> (ppm)			25-125*
CO (ppm)			<25
Stack Oxygen (Vol %)			2.0

WASTES      A) 200,000 lb/hr low oxygen vapor with 400-600 no<sub>x</sub>  
                   B) 4.5 tons/hr of liquid cyanide waste.  
                   C) 3 tons/hr liquid waste with 27% bound nitrogen and 50% water

\* Depends upon waste composition



**TABLE 1**

**THERMAL OXIDIZER / WASTE HEAT BOILER TEST DATA**

<b>Temp.</b> <b>NOx</b> (°F)	<b>Guaranties</b>			<b>I n i t i a l</b>			<b>Final</b>
	<b>NOx</b>	<b>CO</b>	<b>VOC Dest.</b>	<b>NOx</b>	<b>CO</b>	<b>VOC</b>	
	(PPM)	(PPM)	%	(PPM)	PPM		(Dest.%)
	(MM BTU)	(lb/hr)		(MM BTU)	(lb/hr)	(lb/hr)	
1400	-----	-----	-----	8.8	992	99.3	6.2
	-----	-----	-----	0.032	118		0.022
1550	-----	-----	-----	13.8	65	99.99	8.7
	-----	-----	-----	0.046	7.7		.031
1600	-----	140	99	21.1	10	>99.99	12.3
	0.06	16.7		0.06	1.17		0.041
1800	-----	-----	-----	26.7	<0.1	>99.99	20.8
	-----	-----	-----	0.075	<0.01		0.059
2000	-----	-----	-----	40.8	<0.1	>99.99	35.7
	0.097	-----	-----	0.105	<0.01		0.088